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Synthesis and Characterization of Syndiotactic 1,2-Poly(3-methyl-1,3-pentadiene)

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ABSTRACT: 3-Methyl-1,3-pentadiene was polymerized with the system $Fe(bipy)_2Cl_2$−MAO (bipy = bipyridine) obtaining a highly stereoregular polymer. The polymer was completely characterized by IR, NMR (^{13}C, ^{1}H in solution and ^{13}C in the solid state), DSC, and X-ray techniques and found to have a syndiotactic *E*-1,2 structure. The crystalline structure of the polymer was also determined, and comparisons are made with other crystalline 1,2-polydienes. The results were compared with those obtained from other dienes (butadiene, isoprene, 2,3-dimethyl-1,3-butadiene) with the same catalyst, which allowed for new data confirming and supporting what already proposed to interpret the diene polymerization mechanism.

Introduction

We have recently investigated the polymerization of butadiene and other 1,3-dienes with catalysts based on Fe complexes with nitrogen ligands, specifically with $Fe(bipy)_2Cl_2$−MAO and $Fe(bipy)_2Et_2$−MAO (MAO = methylaluminoxane).[1] This investigation is a continuation of a work initiated long ago aimed at obtaining new experimental data in order to improve our understanding of the mechanism of diene polymerization with transition metal catalysts.

It is well-known that one of the characteristics of diene polymerization is that the same catalysts can give polymers of different structure from different monomers. There are several examples in the literature regarding this case. $AlEt_3$−$Ti(OBu)_4$[2] and $CrCl_2(dmpe)_2$−MAO (dmpe = 1,2-bis(dimethylphosphino)ethane)[3] give 1,2 polymers from butadiene, but they give *cis*-1,4 polymers from (*E*)-1,3-pentadiene. $CpTiCl_3$−MAO gives polymers with a predominantly *cis*-1,4 structure from butadiene and (*E*)-2-methyl-1,3-pentadiene, polymers with a mixed 1,2/*cis*-1,4 structure from (*E*)-1,3-pentadiene, and polymers with a syndiotactic 1,2 structure from 4-methyl-1,3-pentadiene.[4] $CoCl_2(PRPh_2)_2$−MAO (R = alkyl or cycloalkyl group) gives 1,2 polymers having isotactic or syndiotactic structure depending on the nature of the group R and on the type of monomer.[5] The dependence of chemo- and stereoselectivity on so many variables complicates the situation, but on the other hand, the relationship between the structure of the monomer and that of the resulting polymers can provide information for a better understanding of the factors determining or affecting chemo- and stereoselectivity.[4b,6]

In preliminary notes we have reported that $Fe(bipy)_2Et_2$−MAO[1a] and $Fe(bipy)_2Cl_2$−MAO[1b] are very active systems for the polymerization of some dienes (butadiene, isoprene, 2,3-dimethylbutadiene, 3-methyl-1,3-pentadiene) and that chemo- and stereoselectivity are strongly dependent on the polymerization temperature. Highly stereoregular polymers from butadiene, isoprene, and 3-methyl-1,3-pentadiene can be obtained only in polymerizations conducted below 0 °C.[1] We have already reported on the characterization of the polymers obtained from butadiene,[1] isoprene,[1,7] and 2,3-dimethylbutadiene,[1,8] which have respectively syndiotactic 1,2, syndiotactic 3,4, and *cis*-1,4 structures.

In this paper we report on the characterization of poly(3-methyl-1,3-pentadiene) and examine the mechanistic conclusions that can be derived from the results obtained with Fe-based catalysts. The crystalline molecular structure of this novel polymer was also determined and compared with those of other 1,2 and 3,4 polydienes (i.e., syndiotactic 1,2-polybutadiene,[9] syndiotactic 3,4-polyisoprene,[7] and syndiotactic *trans*-1,2-polypentadiene[10]). Detailed information on this topic is reported in the forthcoming article.[11]

Experimental Section

Materials. $Fe(bipy)_2Cl_2$ was prepared as reported in the literature.[1b,12] Methylaluminoxane (MAO) (Crompton, 10 wt % solution in toluene) was used as received without further purification. Toluene (Carlo Erba, 99.8% pure) was refluxed over Na for ca. 8 h, then distilled, and stored over molecular sieves under dry nitrogen. 3-Methyl-1,3-pentadiene (Aldrich, 99% pure, mixture of (*E*) and (*Z*) isomers; *E*:Z molar ratio, 80:20; determined by gas chromatography in our laboratory) was refluxed for ca. 2 h over CaH_2, then distilled trap-to-trap, and stored at −30 °C under dry nitrogen.

Polymerization with $Fe(bipy)_2Cl_2$−MAO. Toluene (6 mL), 3-methyl-1,3-pentadiene (2 mL, 1.46 g), and MAO (1.26 mL of toluenic solution, 2×10^{-3} mol) were successively introduced in a dried flask. The solution thus obtained was brought to −30 °C and then $Fe(bipy)_2Cl_2$ (2×10^{-5} mol, 8.8 mL of a 1 mg/mL toluenic suspension) was added. All operations were carried out under dry nitrogen. The polymerization was stopped with methanol containing a small amount of hydrochloric acid after 10 days; the polymer was coagulated and repeatedly washed with fresh methanol and

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Table 1. Polymerization of (*E*+*Z*)-3-Methyl-1,3-pentadiene with Fe(bipy)$_2$Cl$_2$−MAO

polymerization[a]		polymer microstructure[b]					
time (days)	yield (%)	1,2 *trans* %	[rrrr] %	MW[c] (g/mol)	*D*[c]	mp[d] (°C)	identity period (Å)
10	78	∼99	≥95	94000	2.1	242	5.15

[a] Polymerization conditions: toluene, total volume 16 mL; (*E*+*Z*)-3-methyl-1,3-pentadiene, 2 mL; MAO, 2×10^{-3} mol; Fe(bipy)$_2$Cl$_2$, 2×10^{-5} mol; *T*, −30 °C. [b] Determined by ^{13}C and ^{1}H NMR analysis. [c] Molecular weight and molecular weight distribution, determined by GPC analysis. [d] Melting point, determined by DSC analysis.

then dried in vacuum at room temperature (polymer yield, 1.14 g, 78% conversion).

The monomer mixture composition during the polymerization reaction was evaluated from the gas chromatography (GC) analyses of polymer solution samples taken at different polymerization times. The GC analyses were performed on a Hewlett-Packard 6890 Plus instrument equipped with a flame ionization detector. The oven was set at 25 °C for 10 min and then heated to 150 °C at a rate of 5 °C/min. As a separation column, a fused silica capillary column Supelco SPB-5, 30 m × 0.32 mm i.d., with a film thickness of 0.25 μm, was used.

Polymer Characterization. The infrared spectra were recorded on a Bruker IFS 48 instrument; the polymer spectra were obtained as KBr pellets. Differential scanning calorimetry (DSC) analyses were carried out on a Perkin-Elmer Pyris 1 instrument. Typically, ca. 15 mg of polymer was analyzed in each run, under a nitrogen atmosphere, and the scan rate was 20 °C/min.

^{13}C and ^{1}H NMR measurements were carried out on Bruker AM 270 and Avance 400 instruments. The spectra were obtained in $C_2D_2Cl_4$ at 103 °C (hexamethyldisiloxane, HMDS, as internal standard). The concentration of polymer solutions was about 10 wt %.

HSQC (heteronuclear single quantum correlation) experiments were carried out with a delay of 1.9 ms for creation of the antiphase magnetization (corresponding to a $^{1}J_{CH} = 130$ Hz).

HMBC (heteronuclear multiple bond correlation) experiments were carried out with a delay of 100 ms for the evolution of long-range coupling and a delay of 3.4 ms for creation of the antiphase magnetization (corresponding to a $^{1}J_{CH} = 146$ Hz, peculiar of olefinic heteronuclear one-bond coupling constants).

Solid-state NMR ^{13}C experiments were performed using a Bruker AVANCE spectrometer operating at 400 MHz for proton and a 4 mm double bearing MAS probe. The experiments were recorded at room temperature, with 90° pulse lengths of about 4 μs and spinning rate of 5 kHz, and were transformed using a line broadening of 10 Hz. The number of scans (NS) is indicated in the figure captions. For the ^{13}C cross-polarization and magic-angle spinning (CPMAS) NMR experiments, recycle times of 5 s and contact times of 1 ms were used. The spectra select the most hindered, crystalline carbons.

X-ray spectra were obtained using the Ni-filtered Cu Kα radiation ($\lambda = 1.5418$ Å). Powder spectra were collected by a Philips PW3710 automated diffractometer operating in the conventional $\theta/2\theta$ Bragg−Brentano geometry.

Results and Discussion

The polymerization of 3-methyl-1,3-pentadiene (mixture of *E* and Z isomers) with Fe(bipy)$_2$Cl$_2$−MAO gives a polymer with a 1,2 structure. The polymer obtained at room temperature has some degree of crystallinity,[1a] while that obtained at −30 °C (Table 1) is highly crystalline (Figure 1), with a melting point of 242 °C (Figure 2).

The IR spectrum of the polymer is reported in Figure 3. The absence of any band at 911 cm^{-1} excludes a 3,4 structure of the polymer,[13] while the absence of bands typical of isotactic *cis*-1,4 and syndiotactic *cis*-1,4 poly(3-methyl-1,3-pentadiene)[14] (strong bands at 819 and 844 cm^{-1}, respectively) allows us to exclude these types of structures (Figure 4). The presence of a strong band at 810 cm^{-1} is consistent with a 1,2 structure;[1a] however, the IR spectrum alone does not give information concerning the type of configuration of the double bond and the polymer tacticity, iso- or syndiotactic.

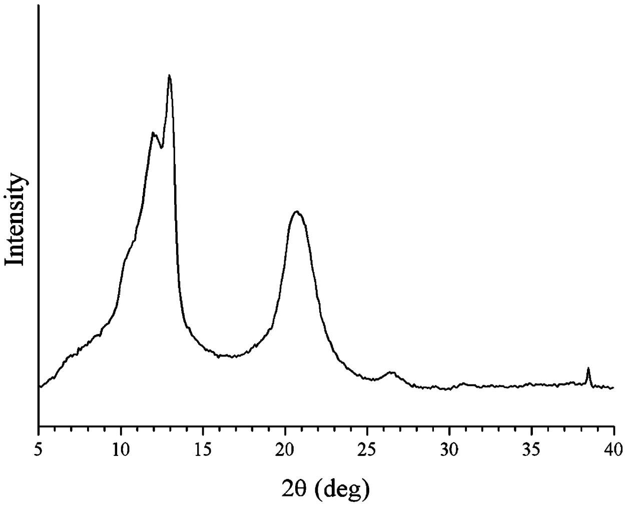


Figure 1. X-ray powder spectrum of the poly(3-methyl-1,3-pentadiene) obtained with Fe(bipy)$_2$Cl$_2$−MAO.

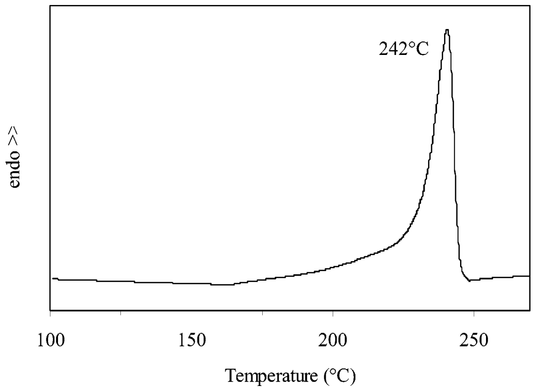


Figure 2. DSC scan of the poly(3-methyl-1,3-pentadiene) obtained with Fe(bipy)$_2$Cl$_2$−MAO.

The crude polymer is poorly soluble even at high temperature; nevertheless, by extracting it in continuous hot toluene for a few hours, we were able to isolate a toluene-soluble fraction (about 60% of the crude polymer). This soluble fraction, exhibiting the same IR spectrum, DSC thermogram, X-ray powder spectrum, and solid-state ^{13}C NMR of the crude polymer, was examined by solution ^{1}H and ^{13}C NMR.

The complete ^{1}H NMR spectrum (Figure 5) assignment was straightforward: methyl protons H6 (intensity 3) at 1.29 ppm, singlet; methyl protons H5 (intensity 3) at 1.44 ppm, doublet since coupled with the adjacent olefin proton; isochronous methylene protons H1 (intensity 2) at 1.03 ppm, triplet due to the coupling with the two H2's; methine proton H2 (intensity 1) at 1.65 ppm, multiplet due to coupling with the H1's; finally, olefin proton H4 (intensity 1) at 4.92 ppm, multiplet due to direct coupling with the H5's (6.4 Hz) and long-range coupling with the H6's and H2.

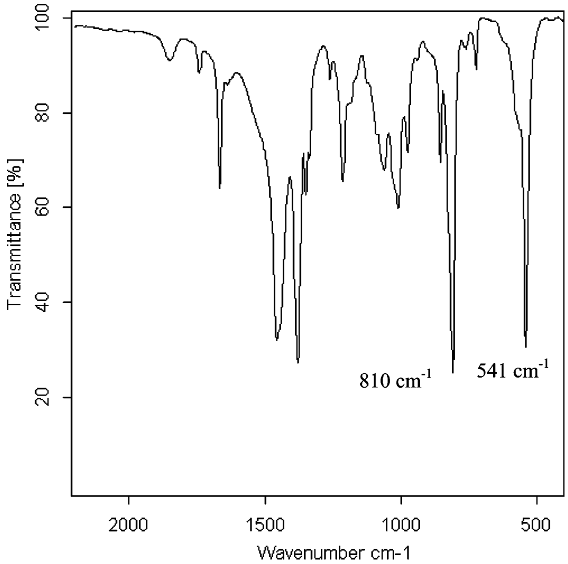


Figure 3. FT-IR spectrum of the poly(3-methyl-1,3-pentadiene) obtained with Fe(bipy)$_2$Cl$_2$−MAO.

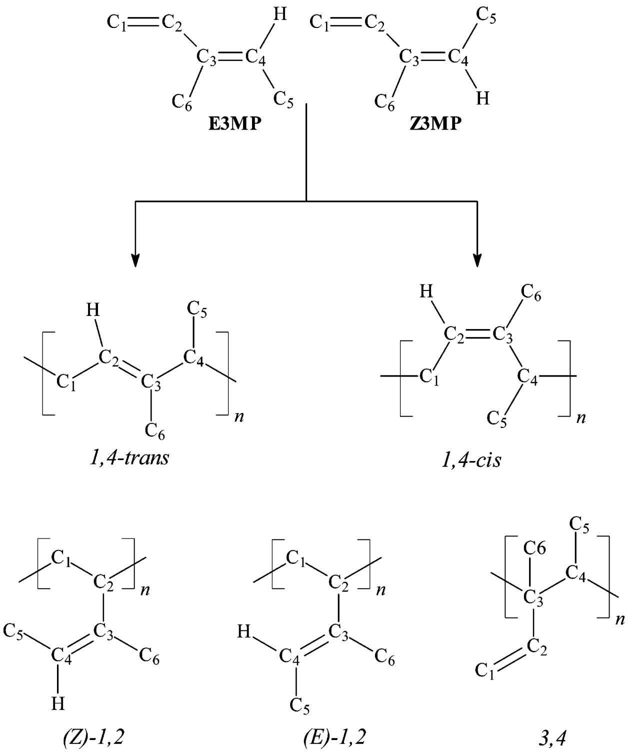


Figure 4. Possible monomer units derived from (*E*+*Z*)-3-methyl-1,3-pentadiene ((*Z*)-1,2 polymer from *Z*3MP; (*E*)-1,2 polymer from *E*3MP).

The ^{13}C NMR (Figure 6) spectrum was assigned on the basis of the chemical shift values and of the multiplicity in the proton coupled spectrum (not reported), which allowed us to distinguish between primary, secondary, tertiary, and quaternary carbons. The ambiguity between the two methyl carbons C5 and C6 has been solved through a HSQC spectrum[15] (Figure 7) which correlates carbons with proton chemical shifts. In fact, the carbon signal at 10.91 shows a correlation with the proton signal (doublet) at 1.44 ppm, while the carbon signal at 9.72 ppm shows a correlation with the proton signal (singlet) at 1.29 ppm.

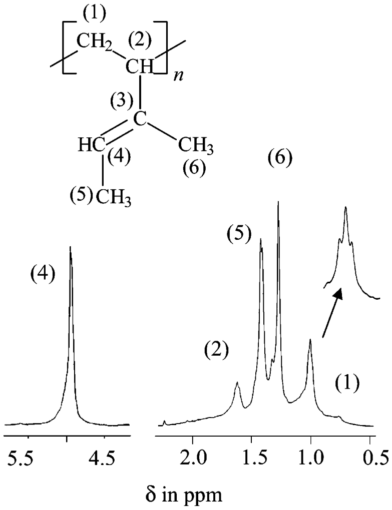


Figure 5. ^{1}H NMR spectrum of the poly(3-methyl-1,3-pentadiene) obtained with Fe(bipy)$_2$Cl$_2$−MAO.

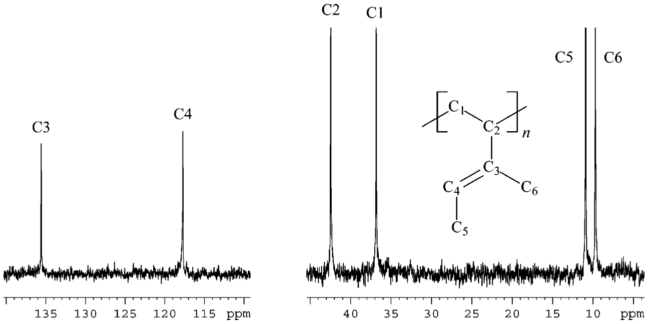


Figure 6. ^{13}C NMR spectrum of the poly(3-methyl-1,3-pentadiene) obtained with Fe(bipy)$_2$Cl$_2$−MAO.

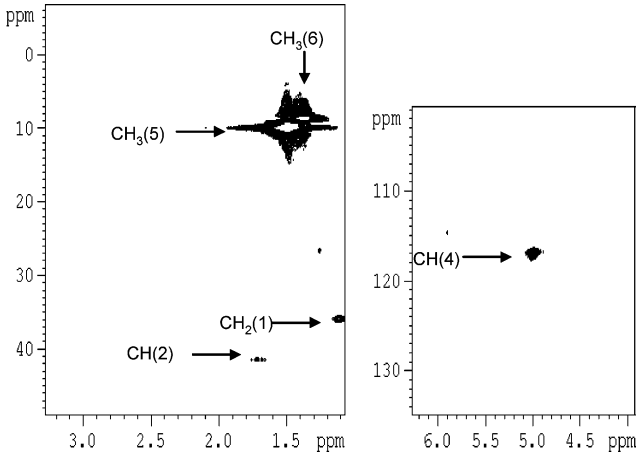


Figure 7. HSQC spectrum of the poly(3-methyl-1,3-pentadiene) obtained with Fe(bipy)$_2$Cl$_2$−MAO.

The presence of a disubstituted alkene carbon (C3, at 135.59 ppm) excludes the 3,4 structure, while it is consistent with 1,2 and 1,4 structures (see Figure 4). It was likewise possible to discriminate between a 1,4 and a 1,2 structure on the basis of the HMBC spectrum[16] (Figure 8).

In a 1,4 structure H5 protons should have two three-bond correlations with C3 (olefinic carbon) and C1 (aliphatic carbon) and H6 protons again two three-bond correlations with C2 (olefinic carbon) and C4 (aliphatic carbon). On the contrary, in a 1,2 structure H5 protons should have only one three-bond correlation with C3 (olefinic carbon) and H6 two three-bond correlations with C2 (aliphatic carbon) and C4 (olefinic carbon). In the HMBC of Figure 8, H5 protons exhibits only one three-bond correlation with C3. The absence of any correlation between H5 and aliphatic carbons is thus consistent with a 1,2

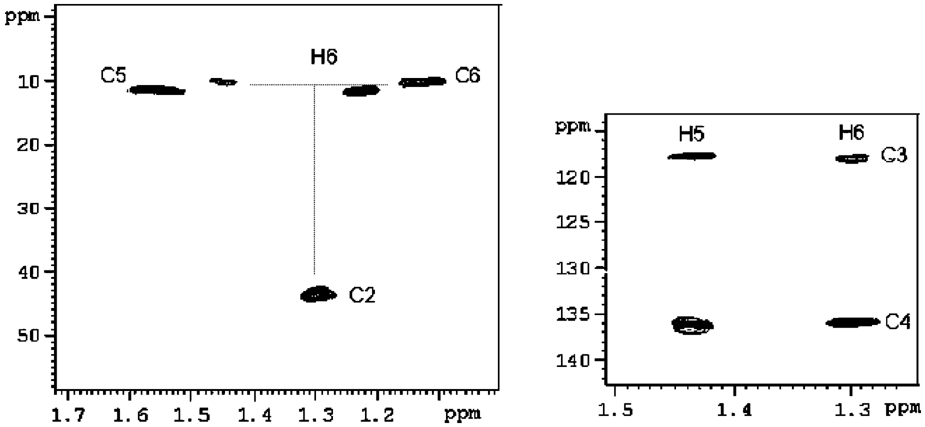


Figure 8. HMBC spectrum of the poly(3-methyl-1,3-pentadiene) obtained with Fe(bipy)$_2$Cl$_2$−MAO.

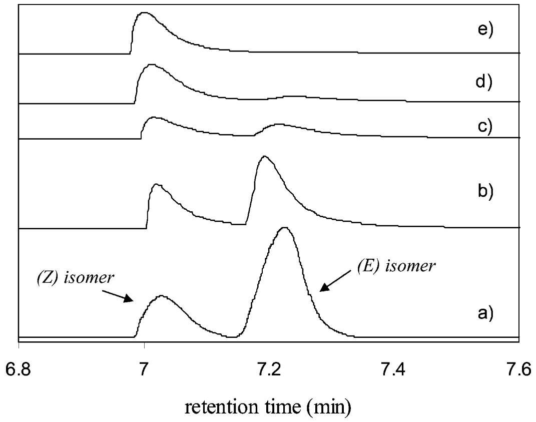


Figure 9. GC chromatograms of the polymerization solution at (a) the beginning of the polymerization (*E*:*Z* molar ratio, 80:20), (b) after 42 h (*E*:*Z* molar ratio, 65:35), (c) after 68 h (*E*:*Z* molar ratio, 55:45), (d) after 139 h (*E*:*Z* molar ratio, 20:80), and (e) after 235 h (*E*:*Z* molar ratio, 0:100).

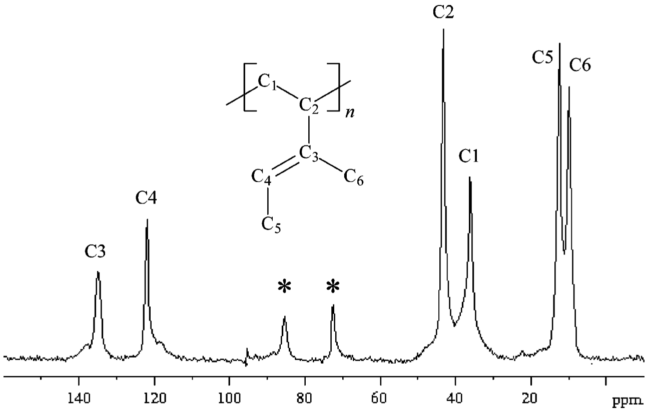
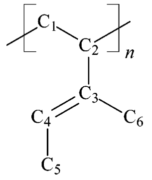


Figure 10. Solid-state ^{13}C CPMAS NMR spectrum of the poly(3-methyl-1,3-pentadiene) obtained with Fe(bipy)$_2$Cl$_2$−MAO. Asterisks indicate spinning side bands.

Table 2. Solution and Solid-State ^{13}C NMR Assignments



carbon	solution ^{13}C δ (ppm)	solid-state ^{13}C δ (ppm)
C1	36.84	36.41
C2	42.47	43.72
C3	135.59	135.22
C4	117.71	122.21
C5	10.91	12.88
C6	9.72	10.25

structure of the polymer under investigation, in good agreement with the IR indication.

Moreover, the experimental chemical shifts observed in the ^{13}C NMR spectrum are very close to those calculated from the spectrum of 1,2-polybutadiene by applying the addition rules,[17] thus further confirming a 1,2 structure.

The monomer used, as reported in the Experimental Section, is a mixture of (*E*) and (Z) isomers (80:20 molar ratio, as indicated by the GC analysis). By monitoring the polymerization solution at different times by gas chromatography (Figure 9), we have found that only the (*E*) isomer is consumed while the (*Z*) isomer is not incorporated in the polymer chain and can be quantitatively recovered at the end of the polymerization by a trap-to-trap distillation. This evidence is supported by the fact that in other polymerization runs, carried out at the same polymerization conditions, the monomer conversion, even after long polymerization time, was never higher than 80%. Moreover, all the polymerizations carried out gave the same results, giving polymers having practically the same melting point (around 242 °C) and X-ray powder spectrum, suggesting indeed a high reproducibility of the polymerization.

Finally, the polymer tacticity can be determined by considering the ^{1}H NMR spectrum of the polymer (Figure 5). It has been reported in the literature that in the ^{1}H NMR spectrum the signal corresponding to the methylene protons is a triplet in a syndiotactic polymer[18] while two different doublet of triplets are observed in the case of an isotactic polymer;[19] the two methylene protons are in fact isochronous in a syndiotactic structure, while they are anisochronous in an isotactic structure. In the spectrum of Figure 5 the signal around 1.03 ppm, corresponding to the methylene protons, is a triplet, in agreement with a syndiotactic structure.

The polymer was also analyzed by ^{13}C NMR in the solid state. The ^{13}C CPMAS spectrum is shown in Figure 10, and the peaks were assigned accordingly to the solution ^{13}C spectrum (Table 2). A single resonance is observed for each carbon, implying a unique environment for chemically equivalent carbons, in agreement with a trans-planar conformation. This was found before for other 1,2-diene polymers such as syndiotactic 1,2-polybutadiene,[9] syndiotactic 3,4-polyisoprene,[7] and syndiotactic *trans*-1,2-polypentadiene.[10]

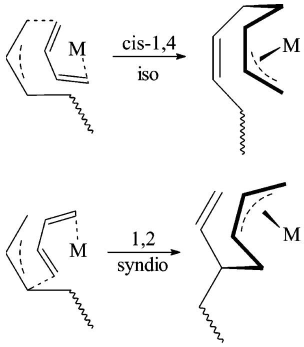


Figure 11. Scheme of formation of isotactic *cis*-1,4 vs syndiotactic 1,2 polymers from 1,3-dienes.

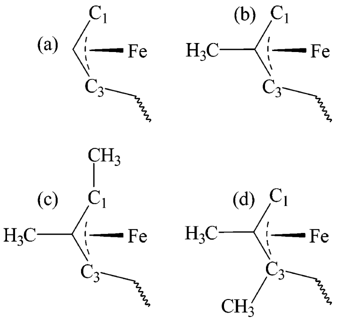


Figure 12. Possible allylic units derived from (a) butadiene, (b) isoprene, (c) 3-methyl-1,3-pentadiene, and (d) 2,3-dimethyl-1,3-butadiene.

The above conclusions regarding the tacticity and the molecular structure of the polymer under investigation are also supported by the X-ray fiber diffraction data of the polymer. In fact, a value of 5.15 ± 0.05 Å was found for the *c* axis, which is consistent with the syndiotactic 1,2 structure of the polymer. Detailed information on the X-ray studies are reported in another paper.[11]

It appears from the NMR and X-ray examination that $Fe(bipy)_2Cl_2$−MAO gives at −30 °C a highly stereoregular syndiotactic 1,2 polymer from 3-methyl-1,3-pentadiene. The same system is also able to give syndiotactic 1,2-polybutadiene and syndiotactic 3,4-polyisoprene at the same temperature;[1] however, these polymers are less stereoregular than the poly(3-methyl-1,3-pentadiene) because they contain 1,4 units (about 10%), which are practically absent in poly(3-methyl-1,3-pentadiene). These results, together with the fact that the same system gives from 2,3-dimethyl-1,3-butadiene a highly crystalline *cis*-1,4 polymer,[1,8] can be interpreted on the basis of the scheme shown in Figure 11, which we have proposed in previous papers for the formation of isotactic *cis*-1,4 and syndiotactic 1,2 polymers from 1,3-dienes.[4,6,20] If we assume that the structures of the allylic units derived from butadiene, isoprene, 3-methyl-1,3-pentadiene, and 2,3-dimethyl-1,3-butadiene are those shown in Figure 12, it appears that in the case of 3-methyl-1,3-pentadiene (Figure 12c) C1 of the allylic unit is more substituted and consequently less reactive than C1 of the allylic groups derived from butadiene (Figure 12a) and isoprene (Figure 12b). It follows that only 1,2 units are formed in the polymerization of 3-methyl-1,3-pentadiene, whereas a certain amount of 1,4 units are formed in the polymerization of butadiene and isoprene. On the other hand, in the allylic unit derived from 2,3-dimethyl-1,3-butadiene, C1 is less substituted than C3 (Figure 12d) and consequently much more reactive, and this is the reason why only *cis*-1,4 units are formed in the polymerization of 2,3-dimethyl-1,3-butadiene.

Conclusions

A novel highly crystalline polymer was obtained by polymerizing 3-methyl-1,3-pentadiene with the system $Fe(bipy)_2Cl_2$−MAO, which was found to have a syndiotactic (*E*)-1,2 structure. The NMR and X-ray characterization of the polymer consistently show that the all-trans main-chain conformation is strongly favored for this polymer. This behavior is closely related to those evidenced for syndiotactic 1,2-polybutadiene,[9] syndiotactic 3,4-polyisoprene,[1,7] and syndiotactic *trans*-1,2 polypentadiene.[10]

The results obtained have also some mechanistic implication, allowing us to confirm some aspects of the diene polymerization mechanism, specifically the role of monomer structure in affecting and determining the polymerization chemoselectivity.

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